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HEAVY METALS ADSORPTION BY XANTHATE OF FOOD PROCESSING WASTE

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Abstract

Industrial effluent loaded with heavy metals are a cause of hazard to human and other forms of life. Conventional methods such as precipitation, evaporation, electroplating, ion exchange, membrane process used for removal of heavy metals from waste water however, are often cost prohibitive having inadequate efficiencies at low metal ion concentrations. Adsorption technology has become one of the alternative treatments. It is observed that appropriated modification of the raw adsorbents especially xanthates can eliminate the drawbacks of adsorbent and improve their performances significantly. Xanthates are most prominent because they are highly insoluble, easy to prepare with relatively inexpensive reagents and have high stability constant values of the metal complexes formed. Xanthates are formed by reacting an organic hydroxyl containing substrate with carbon disulfide under caustic condition. One of organic hydroxyl-containing substrate that can be used for xanthation is food processing waste. The major factors affect the biosorption process are: contact time, initial metal ion concentration, temperature, pH & biomass concentration in solution. It is postulated that metal ion adsorption process could undergo a complex formation. Most of heavy metal adsorption into the xanthate compound followed Langmuir adsorption isotherm model, and well described by the pseudo-second- order equation.

Key-word : Adsorption, Xanthate, Heavy metal

INTRODUCTION

Heavy metal wastewater exists in various industries, such as metal finishing, electroplating, plastics, pigments and mining, which threatens to the environment and human lives severely (Table 1). Therefore, it is urgent to remove those toxic heavy metals from wastewater. Although heavy metal removal from aqueous solutions can be achieved by conventional methods, including chemical precipitation, filtration, oxidation/reduction, electrochemical treatment, evaporative recovery, ion exchange and membrane technologies, they may be ineffective or cost-expensive, especially when the metal ion concentrations in solution are in the range of 1−100 mg/L.

Recently, adsorption technology has become one of the alternative treatments, especially the widespread industrial use of low-cost adsorbents for wastewater treatment is strongly recommended due to their local availability, technical feasibility, engineering applicability and cost effectiveness. However, using the biological adsorbents directly may suffer from lack of specificity and poor adsorption capacity. It is observed that appropriated modification of the raw adsorbents by crown esters, amines, polyethylamine and sulphur bearing groups like sulfides, thiols, dithiocarbamates, dithiophosphates and xanthates can eliminate the drawbacks and improve their performances significantly.

Table 1. General Distribution of Heavy Metals in Particular Industrial Effluents

Industries	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Ti	Zn
General industry and Mining			√	√	√		√		√		√
Plating		√	√	√				√	√		√
Paint Product			√						√	√	
Fertilizer		√	√	√	√	√	√	√	√		√
Insecticides/Pesticides	√			√		√					
Tanning	√		√								
Paper Product			√	√		√		√	√	√	√

Table 2. Chemical Composition of Food Processing Waste

Food Processing Waste	Fibre	Pectin	Lignin	Cellulose
Apple pomace	62,5	15,69	18,2	-
Cocoa pod husk	36,3	6	-	13,7
Pear pomace	43,9	7,05	5,2	-
Lemon Peel	50,9	25,23	5,5	-

Xanthates are most prominent because they are highly insoluble, easy to prepare with relatively inexpensive reagents and have high stability constant values of the metal complexes formed. Xanthates are formed by reacting an organic hydroxyl containing substrate with carbon disulfide under caustic condition (Sha et al., 2010). And the basic chemical reaction of the xantation is shown on Figure 1.

Figure 1. Xanthation reaction

One of organic hydroxyl-containing substrate source is food processing waste. Food processing wastes are the end products of the food processing industries which can not be recycled or used for other purposes. These wastes pose increasing disposal and potential severe pollution problems and represent a loss of valuable biomass and nutrients. The wastes will be considered valuable, if the value of derived products from these wastes exceed the cost of reprocessing. Some xanthate of food processing wastes have been used in heavy metal removal. Homagai et al. (2009) used apple waste xanthate in order to adsorp Pb^{2+}, Cd^{2+}, Zn^{2+}, and Fe^{3+}. Sha et al. (2010) used orange peel xanthate in removal of five heavy metal i.e: Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+}. While apple juice residue xanthate was used in removing lead from aqueous medium (Bashyal, Homagai, & Ghimire, 2010).

Apple pomace and orange peel have been used as raw material for xanthate compound because of their high pectin and cellulose content that made them rich of hydroxyl functional group. Chemical composition of several food processing waste are listed in Table 2.

The common procedure for the production of xanthate compound derived from food processing waste is shown on Figure 2.

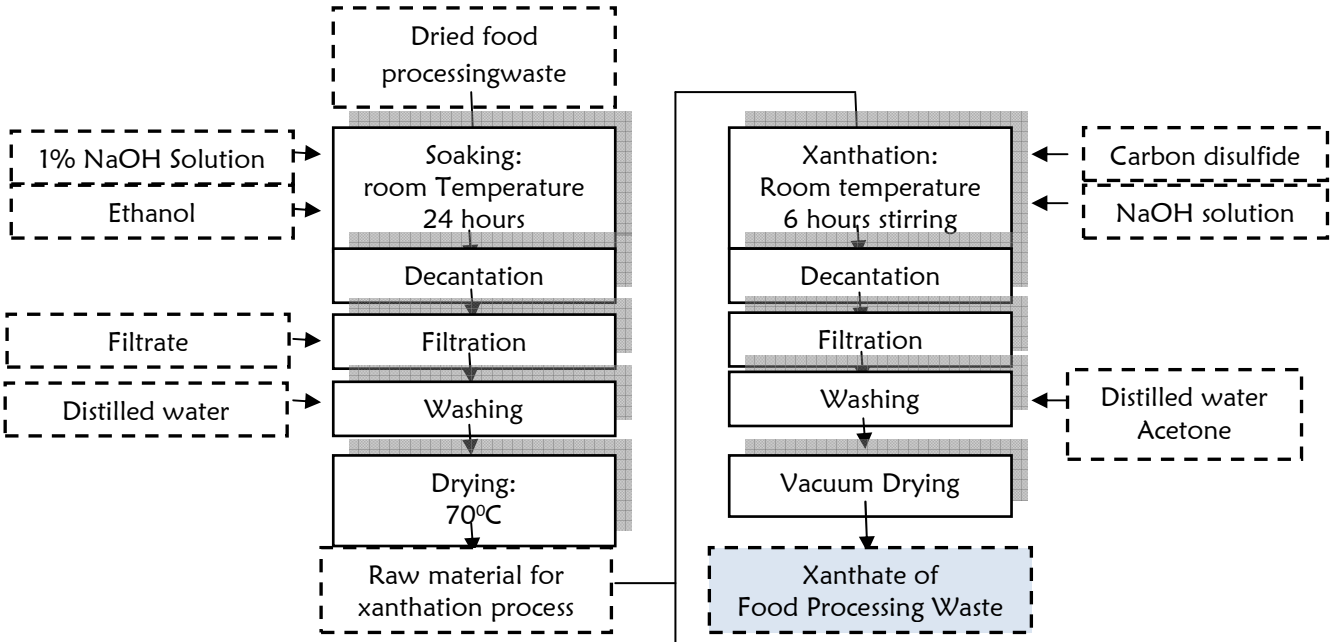

Figure 2. Procedure for the production of xanthate compound derived from food processing waste

Factors affecting heavy metal ions adsorption into xanthate compounds

The major factor that affect the biosorption process are: contact time, initial metal ion

concentration, temperature, pH & biomass concentration in solution (Saravanan et al. (2010).

Adsorption equilibrium of metal ion into xanthate compound can be attained in a varied duration. Adsorption processes of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+} by using orange peel xanthate can attain equilibrium within 20 min (Sha et al., 2010). A similar result showed in Pb^{2+} adsorption by apple juice residue xanthate. The amount of adsorbed Pb^{2+} was increased with contact time and occurred in two stages i.e. initial rapid uptake within 15-20 min followed by subsequent slow uptake, until steady state condition was attained (Bashyal, Homagai, & Ghimire, 2010). A longer equilibrium time was reported by Homagai et al. (2009). Adsorption of Pb^{2+}, Cd^{2+}, Zn^{2+}, and Fe^{3+} ions by using apple waste xanthate were showed that the equilibrium time of all metal ions was above 10 h.

pH is an important parameter for adsorption of metalions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during adsorption (Homagai et al. 2005). The variation of the solution pH is capable of influencing not only the binding site dissociation state, but also the solution chemistry of the target metal in terms of hydrolysis, complexation by organic and/or inorganic ligands and redox potentials. Most research conducted on heavy metal biosorption indicates that the decrease in ion biosorption at acid pH may be due to the increase in competition with protons for active sites. At alkaline pHs, however, other effects may arise that also alter the process, such as the predominant presence of hydrated species of heavy metal, changes in surface charge or the precipitation of the appropriate salt (Saikew & Kaewsarn, 2010).

In the adsorption processes of Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+} by using orange peel xanthate, the percent of adsorbed metal ions increases with the increase in pH, and almost all metal ions can be absorbed to the extent of almost 80%−100% at weakly acidic conditions (Sha et al. 2010). While in the adsorption of Pb^{2+} by apple waste xanthate, the maximum adsorption was obtained at pH 4. The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH, adsorption of Pb^{2+} ions was intensively decreased towards a fixed number of adsorption sites due to high positive charge density of protons on the surface sites. This is a result of competition between Pb^{2+} ions and H_3O^+ for binding sites. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption to get optimum value. (Bashyal, Homagai, & Ghimire, 2010).

Mechanism of Adsorption

The adsorption of heavy metal ion on the surface of xanthate compounds may be regarded as ion- exchange as well as some complexation and or chelation. By ion exchange, two negative charged sulfur atoms of xanthate compounds participate in capturing one divalent metal ion. However, complex formation occurs between four sulfur atoms and one divalent metal ion (Figure 3). It is postulated that metal ion adsorption process could undergo both ion exchange and complex formation. Because most heavy metal belong to transition metals, which have empty orbitals that can be occupied by electrons to form complex and considering steric hindrance, mechanism (b) is the most possible adsorption process (Sha et al, 2010; (Bashyal, Homagai, & Ghimire, 2010).

Adsortion Equilibrium Model

The equilibrium of the adsorption process is often described by fitting the experimental points with models usually used for the representation of isotherm adsorption equlibrium. The two widely accepted and linearised equlibrium adsorption isotherm models for single solute system are given by the following equations:

Langmuir: $$q = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad [1]$$

Where q is the miligrams of metal accumulated per gram of the biosorbent material; C_{eq} is the metl residul concentration in solution; q_{max} is the maximum specific uptake corresponding to the site saturation and b is the ratio of adsorption and desorption rates. This is a theoritical model for monolayer adsorption.

Another impirical model for monolayer adsorption is

Freundlich: $$q = K_F C_{eq}^{1/n} \quad [2]$$

Where K_F and n are constants.These models can be applied at a constant pH and used for modelling of biosorption equilibrium in the presence of one metal.

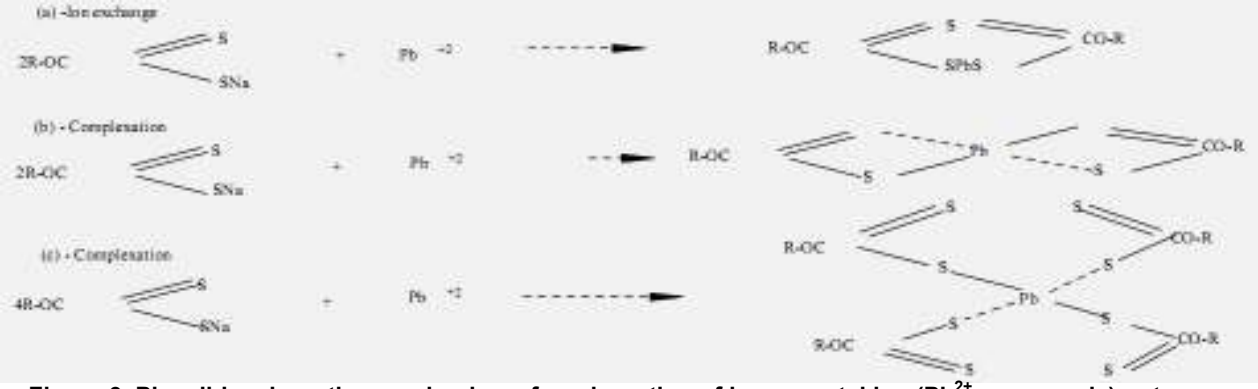

Figure 3. Plausible adsorption mechanisms for adsorption of heavy metal ion (Pb^{2+} as example) onto xanthate compound

Some researchs revealed that heavy metal adsorption into the xanthate compound followed Langmuir adsorption isotherm model. Homagai et al. (2009) used apple waste xanthate in order to adsorp Pb^{2+}, Cd^{2+}, Zn^{2+}, and Fe^{3+}. The Langmuir biosorption isotherm parameter and correlation coefficient for adsorption of metal ions onto xanthate of apple waste are listed in Table 3.

Table 3. The Langmuir isotherm parameter for adsorption of metal ions onto xanthate of apple waste

Metal ions	Q_{max}(mg/g)	b(l/mg)
Pb^{2+}	250,00	0,064
Cd^{2+}	192,30	0,064
Zn^{2+}	123,45	0,040
Fe^{3+}	62,89	0,032

Sha et al. (2010) used orange peel xanthate in removal of five heavy metal i.e: Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, and Ni^{2+}. The Langmuir biosorption isotherm parameter and correlation coefficient for adsorption of metal ions onto xanthate of orange peel are listed in Table 4.

Table 4. The Langmuir isotherm parameter for adsorption of metal ions onto xanthate of orange peel

Metal Ions	Q_{max}(mg/g)	b(l/mg)
Cu^{2+}	77,60	0,149
Cd^{2+}	76,57	0,058
Pb^{2+}	218,34	0,056
Zn^{2+}	49,85	0,137
Ni^{2+}	15,45	0,100

The Langmuir biosorption isotherm parameter and correlation coefficient for adsorption of Pb^{2+} onto xanthate of apple juice residu are listed in Table 5 (Bashyal, Homagai, & Ghimire, 2010).

Table 5. The Langmuir isotherm parameter for adsorption of Pb^{2+} onto xanthate of apple juice residu

pH	Q_{max} (mmol/g)	b(l/mmol)
3,5	1,06	11,91
4	1,22	27,91
4,5	1,12	13,61

Sorption Kinetics And Intraparticle Difussion Models

The kinetics of heavy metal ions adsoprtion on food processing wastes xanthate can be analysed using Pseudo first order, Pseudo-second order and intraparticle diffusion kinetic models. The conformity between experimental data and the model predicts values that expressed by correlation coefficients (R^2 values close or equal to 1). A relatively high R^2 value indicates that the model succesfully describes the kinetics of the adsorption process (Iqwe& Abia, 2007; Odoemelam, Iroh, & Iqwe, 2011)

Pseudo-first order kinetic model

The pseudo-first order equation is generally expressed as follows:

$$dq_t/_{dt} = K_1(q_e - q_t) \quad [3]$$

Where $q_e and\ q_t$ are adsorption capacity at equilibrium and time t, respectively (mg g^{-1}), K is the rate constant of Pseudo-first adsorption (L min^{-1}). After integration and applying boundary condition t=0 to t-t dan $q_t = 0\ to\ q_t = q_t$, the integrated form of equation [3] becomes:

$$\log(q_e - q_t) = \log(q_e) - K_1\, t/_{2,303} \quad [4]$$

When the values of $\log(q_e - q_t)$ are linearly correlated with t and a plot of log $(q_e - q_t)$ versus gives a straight line than we have a good fit for the Pseudo-first order kinetics model. K_1 and q_e are determined from the slope and intercept of the plots , respectively. The higher the K_1 value means the greater the adsorption.

Pseudo-second order kinetics model

The pseudo second adsorption kinetic rate equation is expressed as:

$$dq_t/_{dt} = K_2(q_e - q_t)^2 \quad [5]$$

Where K_2 is the rate constant of Pseudo-second adsorption (g/mg/min). After integration and applying boundary condition t=0 to t-t dan $q_t = 0\ to\ q_t = q_t$, the integrated form of equation [5] becomes:

$$1/(q_e - q_t) = 1/(q_e) - K.t \quad [6]$$

This is the integrated rate law for a Pseudo second order reaction. Equation [6] can be rearranged to obtain equation [7] which has a linear form:

$$tq_t = (1/K_2 q_e^2) + t/q_e, \quad [7]$$

If the initial adsorption rate h is:

$$h_0 = K_2 q_e^2 \quad [8]$$

Then the combination of equation [7] and [8] will give us:

$$tq_t = (1/h_0) + t/q_e, \quad [9]$$

The plot of t/q_t versus t, using equation [7] should give a linear relationship from which q_e and K_2 are determined from the slope and intercept of the plots, respectively.

The heavy metal ion adsorption by xanthate compounds showed that the adsorption process are well described by the pseudo-second- order equation, indicating the process mechanism to be chemical adsorption (Bashyal, Homagai, & Ghimire, 2010; Sha et al., 2010).

Conclusion

Heavy metal of industrial effluent must be removed because its potential hazard to human and other forms of life. Xanthate of food processing wastes are proved to be a good candidate in adsorbing heavy metal ions. The major factors affect the biosorption process are: contact time, initial metal ion concentration, temperature, pH & biomass concentration in solution. It is postulated that metal ion adsorption process could undergo a complex formation. Most of heavy metal adsorption into the xanthate compound followed Langmuir adsorption isotherm model, and well described by the pseudo-second- order equation.

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